Structure, IR and Raman Spectra of the *N*—[4—(Octan—2—Yloxy)Benzyl]—*N,N*—Dimethyl—Hexadecane—1—Aminium Molecule – Promising Object for Liquid Crystal Systems

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The N-[4-(Octan-2-Yloxy)Benzyl]-N,N-Dimethyl-Hexadecane-1-Aminium (N4OYBDHA) molecule contains 97 atoms: 62 hydrogen atoms, 33 carbon atoms, 1 nitrogen, and 1 oxygen atoms. Since the N4OYBDHA molecule contains many atoms, the finding of its equilibrium configuration was carried out in several stages. First of all the molecular geometry was optimized at the HF/cc-pVDZ level of theory. Then optimized geometrical parameters were used for finding equilibrium configuration at the B3LYP/cc-pVDZ level of theory. At the last stage, these optimized parameters were used for geometry optimization at the B3LYP/cc-pVTZ level of theory. The equilibrium geometry of the N4OYBDHA molecule is shown in Fig.1.

According to calculations, the longitudinal and transverse dimensions of the molecule turn out to be 36 and 7 Å, respectively. The value of the dipole moment is 12.9 Debye and it is directed along with the carbon skeleton of the molecule.

As far as the carbon chain is flexible enough it is obviously the N4OYBDHA molecule can exist in lot of conformations. In most stable configuration the carbon chain contains only trance— arrangement of carbon atoms. Less stable conformations may contain gauche— arrangement of carbon atoms. At least three another conformers with one gauche fragment were found for the analyzed molecule (see Fig.2,3,4). The structures of all of them were optimized at the B3LYP/cc-pVTZ level of theory. The most interesting properties of all conformers are represented in Table 1. One can see the energy differences between four conformers are not too high. That means at the room temperature all of them can exist in mixtures. However first conformer has to dominate.

Fig.1. Equilibrium configuration of the N4OYBDHA molecule calculated at the B3LYP/cc-pVTZ level of theory

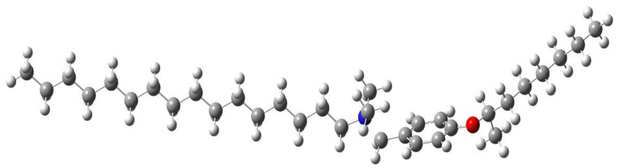


Fig.2. Equilibrium configuration of the second conformer of the N4OYBDHA molecule calculated at the B3LYP/cc-pVTZ level of theory

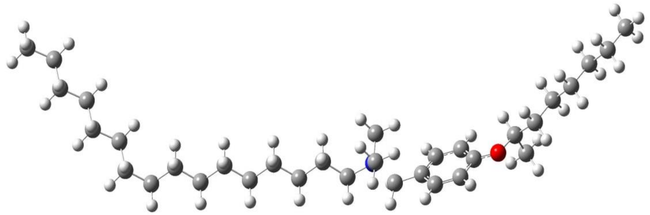


Fig.3. Equilibrium configuration of the third conformer of the N4OYBDHA molecule calculated at the B3LYP/cc-pVTZ level of theory

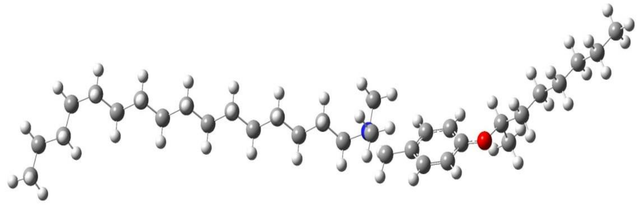
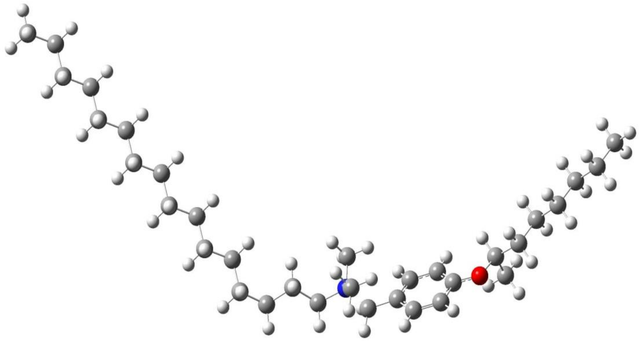


Fig.4. Equilibrium configuration of the third conformer of the N4OYBDHA molecule calculated at the B3LYP/cc-pVTZ level of theory



Using equilibrium geometries of the all conformers of the N4OYBDHA molecule IR and Raman spectra were calculated at the B3LYP/cc-pVTZ level of theory. Due to N4OYBDHA molecule contains 21 methylene (CH_2) groups the large number from the 285 normal modes are a) scissoring, twisting, wagging, and rocking vibrations of these groups as well as
b) stretching vibrations of the C—C and C—H bonds.

However, most of the a) types vibrations produced very weak IR bands and Raman lines. Calculated IR and Raman spectra of the first conformer of the N4OYBDHA molecule are presented in Fig. 5. The IR and Raman spectra of the 2, 3, and 4 conformers are very similar to the ones of the 1 conformers. However few spectral regions demonstrates show spectral differences for different conformers. In particular the 1290—1350 cm^{-1} spectral region is sensitive to configuration to the carbon chain in IR spectrum (see Fig.7), while 2980—3050 cm^{-1} spectral region is sensitive to configuration to the carbon chain in Raman spectrum (see Fig.8).

Table 1. Relative energies and values of dipole moments of four conformers of the N4OYBDHA molecule

Conformer number	Energy [Hartry]	Relative energy [cm^{-1}]	Dipole moment values [Debay]
1	-1425,16968249	0	12,91
2	-1425,16822102	320,0	12,19
3	-1425,16822677	319,5	12,28
4	-1425,16837888	286,1	14,35

Fig.5. Calculated at the B3LYP/cc-pVTZ level of theory IR and Raman spectra of the first conformer of the N4OYBDHA molecule

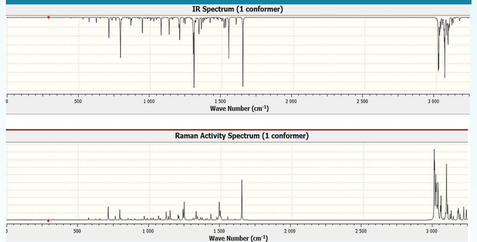


Fig.6. Calculated at the B3LYP/cc-pVTZ level of theory IR spectra of the 1,2, and 3 conformers in the 1290-1350 cm^{-1} spectral region

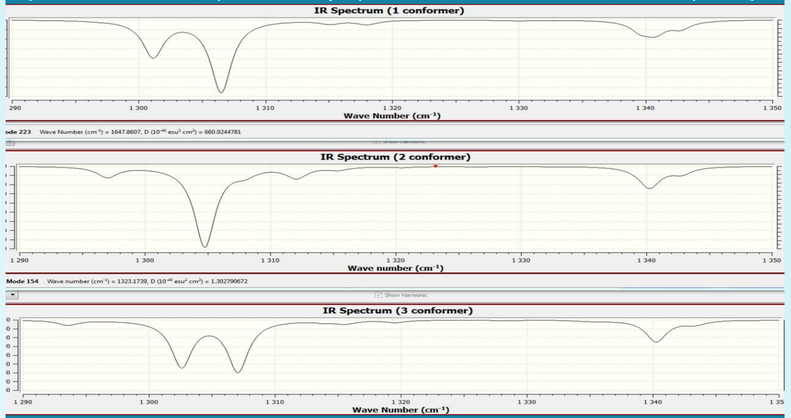


Fig.7. Calculated at the B3LYP/cc-pVTZ level of theory Raman spectra of the 1,2, and 3 conformers in the 2980-3050 cm^{-1} spectral region